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(54) **Multiple layer films and packages made therefrom.**

(57) A multiple layer film (10) is useful in packaging, and the packages (26) in the form of pouches are made therefrom. A first layer (14) of the film is a material containing an ester group, a polycarbonate or a polyether block amide copolymer. A second layer (12) of the film is a sealant, preferably polypropylene polymer blended with an elastomeric styrene ethylene butylene styrene copolymer. A third layer (16) is disposed between the first and second layers and functions as an adhesive, the third adhesive layer typically being either a polypropylene modified with a carboxy group such as an organic acid or anhydride or a styrene ethylene butylene styrene copolymer.

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FIG.1

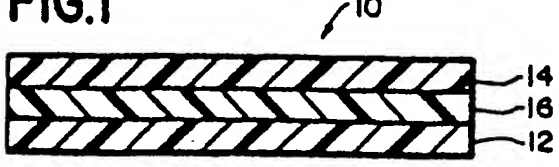
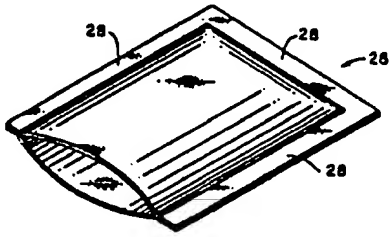


FIG.2



"MULTIPLE LAYER FILMS AND PACKAGES MADE THEREFROM"

This invention pertains to packaging, particularly to packaging liquid in sealed flexible pouches, or bags, where excellent visibility of the contents is desired.

Further, the invention relates to multiple layer films and packages made therefrom.

A particular utility for such packaging is in the packaging of powders, liquids and solutions used for medical services. It is deemed important that the package, including any seals, be strong to prevent contamination, or loss of the contained product. The packaging material should have excellent clarity for observation of the product, and should provide resistance to transmission of moisture vapor. The packaging material should be highly flexible without susceptibility to cracking or stress cracking, and also should be resistant to abuse such as by abrasion, shock impact, or penetration. Finally, since some medical liquids and solutions are processed at high temperatures of up to about 250°F (121°C), it is important that the packaging material be able to tolerate such processing temperature without being adversely affected.

Liquids and solutions for medical use have been packaged in glass bottles and in bags made from polyvinyl chloride with some degree of success. But these packages tend to be somewhat deficient, particularly in regard to abuse resistance, moisture transmission and flexibility. However, no better packaging material has been available, and so PVC and glass have continued to be used despite their deficiencies.

It is an object of this invention to provide an improved multiple layer film for use in packaging, especially liquids and solutions.

We have sought to provide such a film which is highly tolerant of high temperature processing and which shows excellent tolerance of abuse such as abrasion, shock or penetration.

We have also sought to provide improved packages, made from multiple layer films, wherein the packages are useful for packaging liquids and solutions which may require high temperature processing, and wherein the packages may be subject to abusive handling or other adverse handling effects.

Finally, we have sought to provide improved closed and sealed packages which have been subjected to high temperature processing at up to about 250°F (121°C), for up to e.g. about 30 minutes. These packages should not unacceptably be adversely affected by the processing and should retain excellent properties of clarity, flexibility, and integrity. As used herein, the term "package" refers to containers of all types, including pouches.

According to the present invention, there is provided a multiple layer film, comprising:

(a) a first layer, the composition of said first layer being selected from polyesters, copolyesters, polycarbonates and polyether block amide copolymers;

(b) a second sealant layer the composition of which comprises a blend of a propylene polymer and a styrene ethylene butylene styrene copolymer; and

(c) a third adhesive layer adhering the first and second layers together with good adhesion, the third layer being positioned between, and adhered, in face-to-face contact, to the first and second layers.

The invention also provides a package having a wall made from a multiple layer film, which film comprises:

(a) a first layer, the composition of said first layer being selected from polyesters, copolyesters, polycarbonates and polyether block amide copolymers;

(b) a second, sealant layer the composition of which comprises a blend of a propylene polymer and a styrene ethylene butylene styrene copolymer; and

(c) a third adhesive layer adhering the first and second layers together with good adhesion, the third layer being positioned between, and adhered, in face-to-face contact, to the first and second layers.

Multiple layer films according to this invention have a first layer made of an abuse resistant material, preferably containing ester groups, such as polyesters [e.g., polyethylene terephthalate (PET) and polybutylene terephthalate (PBT)] and copolyesters [e.g., glycol modified polyethylene terephthalate (PETG) and PCCE 9967]. Herein, such ester containing materials are sometimes referred to as "EGM's". Alternatively, the material of the first layer may be a polycarbonate ("PC") or polyether block amide copolymer - (PEBA). The sealant layer comprises a first component of a polypropylene and a second component of a styrene ethylene butylene styrene copolymer (SEBS). The third layer is an adhesive and is positioned between, and in face-to-face adherent contact with the first and second layers. Where the first layer is an EGM, the preferred adhesive is styrene ethylene butylene styrene copolymer. A carboxy modified olefin -

(e.g., where the olefin may be polypropylene), is a preferred alternative adhesive where the composition of the first layer is PEBA because the carboxy modified adhesive gives higher levels of adhesion than does SEBS. In preferred carboxy modified polypropylene adhesives, the carboxy modification is an organic anhydride.

In order to achieve the combination of properties of high temperature tolerance and abuse tolerance, the composition of the second, sealant layer is preferably a blend of about 40% by weight to about 90% by weight of the polypropylene and about 60% by weight to about 10% by weight of the styrene ethylene butylene styrene copolymer.

The films according to the invention are readily useful for making packages and pouches, especially by employing heat seals in package formation and closure. For those packages having high fractions of polypropylene in the second layer, the packages are tolerant of high temperature processing, especially up to at least about 250°F (121°C) for a period of up to at least about 10 minutes, preferably at least about 30 minutes.

Embodiments of the invention will now be explained in more detail, by way of example only, in the following description to be read in conjunction with the accompanying drawings, in which:

FIGURE 1 is a cross-section of a portion of a representative multiple layer film according to this invention;

FIGURE 2 is a pictorial view of an open package embodying this invention, which is formed from a multiple layer film according to this invention;

and

FIGURE 3 is a pictorial view of a closed and sealed package formed from a multiple layer film according to this invention.

The details of the invention are most easily seen and understood in relation to the drawings. In FIGURE 1, the overall multiple layer film is designated at 10. The composition of layer 12 is a combination of polypropylene and SEBS. Layer 14 is an abuse resistant polymer composition. Layer 16 is an adhesive material capable of joining layers 12 and 14 with good adhesion.

FIGURE 2 shows a pouch-type package made from multiple layer film of the invention such as that seen in FIGURE 1. The package is made by first bringing portions of the film 10 into facing relationship, with their respective layers 12 facing each other. The enclosure is made by forming seals at 28 about the common periphery of the facing films, leaving one side open for access as seen in FIGURE 2. As shown, layers 12 form the inside surface of the package, and the layers 14 generally form the outside surface of the package.

The closed package of FIGURE 3 is representative of packages of the invention after the final seal 28A has been made.

Alternately, the sheet may be made into a tube by forming a longitudinal seal along overlapping edges, and a transverse seal is also formed across the width of the tube; all as described, for example, in US-A-4,521,437, herein incorporated by reference. This process is particularly suitable for use in vertical form, fill and seal machines.

The functioning of films and packages of the present invention is dependent on the ability of each layer to perform its functions, and the ability of the combined layers to act together. In preferred embodiments, layer 12 primarily serves the function of a heat seal layer. Again in preferred embodiments, the primary function of the layer 14 is to protect the package from external abuse at the package surface, such as by abrasion, cutting, or puncture. Finally, the primary function of layer 16 is to serve as an adhesive to join layers 12 and 14 to each other. The combined effect of the layers is a multiple layer film having strong resistance to external abuse, tolerance for high process temperatures, good unitary identity provided by good interlayer adhesion, and strong heat seals when formed into a package. Those embodiments having copolyester in the first layer, further, have improved clarity.

A preferred minimum thickness for layer 12, for achieving strong heat seals, is about 1 mil (0.025 mm), so that is a preferred minimum thickness. Thicker heat seal layers usually provide more efficient use of the heat seal material, up to about 10 mils (0.25 mm) and that is a generally preferred maximum thickness. While layer 12 may be thicker, and same is encompassed by the scope of the invention, usually no material benefit is seen to be derived from extra thickness of this material, so the greater thicknesses are not generally preferred.

Polypropylene is advantageously used in layer 12 becaus of the combination of properties whereby it forms strong heat seals, contributes to impeding moisture vapor transmission and is tolerant of high temperatures to which a package may be subjected as in retort processing of up to at least about 250°F - (121°C) for process times up to at least about 30 minutes. While th se properties of polypropylene are advantageous and favourable to its use, its brittl ness is disadvantageous. This property is particularly of

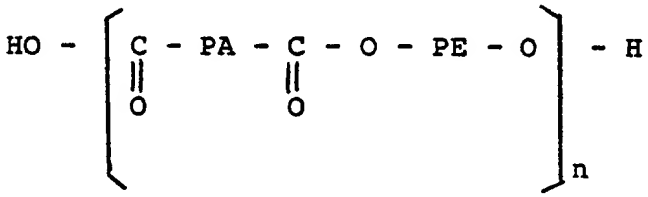
concern because the packages are subjected to high temperature processing, and packaging having polypropylene layers without SEBS blended therein exhibit increased brittleness after the high temperature processing. Moreover, because the polypropylene is present as such a significant proportion of the package composition, the brittleness of the polypropylene markedly tends to influence the overall brittleness of the package. The overall brittlen ss of a package is, of course, a property which is a composite of the brittlenesses of the individual layers, interfacial bond strengths, the elasticity of adjacent layers, and their capability to absorb and dissipate physical shock; and any overwhelming brittleness of any one layer. The composite brittleness of packages may generally be observed as the fraction of the filled and sealed packages which fail after being subjected to physical stress or shock.

In overcoming the problem of brittleness of the polypropylene in packages of the invention, a number of factors work together in combination. Important to achieving the objectives of the invention is the incorporation in the layer 12 of the elastomeric SEBS polymer.

Another factor in controlling the brittleness of layer 12, and thus, in large part, the brittleness of the package, is the selection of the particular polypropylene to be used in layer 12. While any of the polypropylenes may be used as the first component of the blend forming layer 12, polypropylenes which are copolymers having about 2 to about 8 mole percent ethylene are preferred. The copolymer, itself, provides some minimum level of additional resilience in the polypropylene, as compared to a homopolymer. The term "polypropylene" as used herein is intended to include homopolymers and copolymers except where specified otherwise. Whether the polypropylene is a homopolymer or a copolymer, its resilience, whether retort processed or not, is enhanced substantially by the incorporation of the SEBS component. Without the incorporation of the SEBS, the polypropylene homopolymer or copolymer is at least somewhat brittle, and is not as successfully functional as are films of the invention which have this copolymer in layer 12.

While the incorporation of virtually any amount of SEBS into the layer 12 composition will provide some benefit, generally, improvements in the functional performance of the 3-layer film are detected at a level of about 2% by weight of the SEBS in the composition of layer 12. While up to about 90% SEBS may be used in the composition of layer 12, the most desired balance of properties is achieved when the SEBS is present in this layer in an amount of about 10% to about 35%.

PEBA copolymers useful in layer 14 of this invention contain blocks of polyamide and polyether moieties in the polymer chain. A general formula for those polymers is:



PA = polyamide

PE = polyether

The polyamide component may be any of the conventional polyamides, such as nylon 6, nylon 66, nylon 6/66, nylon 6/36, nylon 11, and nylon 12. The polyether component is usually, but not necessarily, selected from polyoxyethylene, polyoxypropylene, and polyoxytetramethylene. The melting point of known PEBA's is about 248°F to about 402°F (120 to 206°C), and the Shore Hardness is about 25 D to about 63 D. Preferred PEBA's are sold by Ato Chemie under the tradename PEBAX. Typical of At Chemie's polymer resins is PEBAX 4033 which has a melting point of about 334°F (168°C) and Shore Hardness of about 40D. Other known commercially available PEBA's are PEBAX 5512 and PEBAX 3533. PEBAX 5512 has a melting point of about 383°F (195°C) and a Shore Hardness of about 55D. PEBAX 3533 has a melting point of about 306°F (152°C) and a Shore Hardness of about 35D.

A sel cted PEBA should have a softening point temperature above the maximum temperature to which it will be exposed during its expected life. Thus, where the film will be subjected to retort proc ssing, as at about 250°F (121°C), th selected PEBA should have softening point temperature above about this temperature.

As indicated above, a highly preferred composition for layer 14 is EGM, and especially a soft copolyester. Softer materials are preferred in layer 14 because films made with th m are mor flexible. A highly preferred, and softer, and especially clear, copolyester is available from Eastman Kodak Company, of Rochester, New York as Eastman PCCE 9967. Layer 14 can also contain PC. Eastman PCCE 9967 is a glycol modified cyclohexanedimethanolcyclohexanedicarboxylate.

By virtue of the interdependence of the several layers on each other for the overall functional performance of the multiple layer film, especially as regards shock abuse, for a given level of functional performance, selection of the specific materials for layer 14 is somewhat dependent on the composition of sealant layer 12. To the extent sealant layer 12 has a high level of resilience by use of polypropylene copolymer, rather than homopolymer, a harder, and thus tougher, material may be selected for layer 14. Where layer 12 has a lower level of resilience, the material chosen for the composition of layer 14 may be softer, thereby obtaining some added resilience for the multiple layer film, albeit at the cost of a possible reduction in abuse resistance for layer 14. Thus can the composition of layers 12 and 14 be adjusted somewhat to compensate one for properties of the other, while achieving the overall desired results for the film as a whole.

Typical of some of the materials used for adhesive layer 16 are the carboxy modified polymers sold by Norchem as Plexars, by DuPont as CXA's and by Mitsui Petrochemical as the Admer series. Where layer 12 has a high fraction of polypropylene, and layer 14 is PEBA, suitable materials for use in layer 16 are carboxy modified polypropylenes such as Admer QF-500, QF-550 and QF-551. Where layer 14 is an EGM, a particularly favourable material for use in layer 16 is an SEBS. Where adequate adhesion is achievable, SEBS is generally preferred over carboxy modified polymers because of its better acceptance by regulators of food and drug substances and packaging therefor. The selection of the adhesive polymer for layer 16 is limited only by the functional requirement that it have good adhesion, after retort, to layers 12 and 14 in the multiple layer film.

Overall, the thickness of the three layers of the films of the invention usually ranges from about 1.5 mils to about 20 mils (0.038 to 0.50 mm), with a preferred range of about 6 mils to about 12 mils (0.15 to 0.30 mm). At the lower limit of about 1.5 mils (0.038 mm), layer 12 is at its usually minimally effective thickness of about 1 mil (0.025 mm). Layer 14 is about 0.4 mil (0.01 mm) which is about its minimal effective thickness for providing abuse resistance. Layer 16 at about 0.1 mil (0.0025 mm) is essentially just thick enough to form a continuous layer. While a film about 1.5 mils (0.038 mm) thick is functional for applications requiring minimal abuse tolerance, higher levels of strength are usually preferred.

Toward the thicker end of the thickness range, films thicker than about 20 mils (0.50 mm) tend to be less flexible due to the overall film thickness, and thus are not preferred.

Preferred films are therefore those having a thickness of about 6 to about 12 mils (0.15 to 0.30 mm), especially about 8 mils (0.20 mm). Within this preferred family of films, preferred ratios of the thicknesses of the layers to the overall thickness of the three layer composite are about 60% to about 85% layer 12, about 5% to about 30% layer 14 and about 10% layer 16. A highly preferred film is about 77% layer 12 as a blend of PPE and SEBS, about 13% layer 14 as copolyester, and about 10% layer 16 as SEBS.

The invention will be explained further by reference to the following non-limiting examples.

EXAMPLE 1

A composition is selected for layer 12 which is about 80% polypropylene and about 20% styrene ethylene butylene styrene copolymer. The composition selected for layer 14 is polyether block amide PEBAX 4033. The composition selected for layer 16 is Admer QF-550. Using these selected materials, a three layer film as in FIGURE 1 is coextruded using three extruders and a multiple layer combining slit die, to form a three layer film. The throughput at the die is so adjusted that the overall layer thickness ratios are about 70% layer 12, about 20% layer 14, and about 10% layer 16. Overall thickness of the film is about 10 mils (0.25 mm).

EXAMPLE 2

A thr e layer film is made as in EXAMPLE 1 xcept that Admer QF-551 is substituted for Admer QF-550.

EXAMPLE 3

A three layer film is made as EXAMPLE 2 except that the layer ratios are about 80% layer 12, and about 10% each for layers 14 and 16.

EXAMPLE 4

A three layer film is made as in EXAMPLE 2 except that the overall thickness of the film is about 8 mils (0.20 mm) and the layer thickness ratios are about 77.5% layer 12, about 12.5% layer 14 and about 10% layer 16.

EXAMPLE 5

A three layer film is made as in EXAMPLE 2 except that the overall thickness of the film is about 8 mils (0.20 mm) and the layer thickness ratios are about 65% layer 12, about 25% layer 14 and about 10% layer 16.

EXAMPLE 6

A three layer film is made as in EXAMPLE 1 except that PEBAX 5512 is used in place of PEBAX 4033.

EXAMPLE 7

A three layer film is made as in EXAMPLE 1 except that SEBS is used in layer 16 in place of Admer QF-550.

EXAMPLE 8

A three layer film is made as in EXAMPLE 1 except that glycol modified cyclohexanedimethanol-cyclohexanedicarboxylate PCCE 9967 is used in layer 14 in place of PEBAX 4033 and SEBS is used in layer 16 in place of Admer QF-550, with the layer thickness ratios being about 77.5% layer 12, about 12.5% layer 14 and about 10% layer 16. The overall thickness of the film was about 8 mils (0.20 mm).

The films made according to EXAMPLES 1-8 were made into heat sealed pouches. The pouches all had good clarity, strength, abuse and shock tolerance, and tolerance of high temperature processing conditions at about 250°F (121°C) for about 30 minutes. The pouches of EXAMPLE 8, using PCCE 9967, had the best clarity.

It must be appreciated that additional layers may be added to the three layer films according to the invention, thereby to impart additional or improved functional properties to the films, or to adapt them to other uses. The invention is not limited to films having but three layers, therefore.

Thus, it will be seen that the invention provides multiple layer films and packages which have a combination of tolerance for significant shock abuse, as well as tolerance of high temperature processing. The films and packages exhibit good heat seal capability and excellent clarity, as well as good barrier properties to transmission of moisture vapor. Further, the packages are excellent for containing liquid products which need protection from abuse and contamination by the outside environment and are especially suitable for containing medical solutions.

Claims

1. A multiple layer film, comprising:

(a) a first layer, the composition of said first layer being selected from polyesters, copolyesters, polycarbonates and polyether block amide copolymers;

(b) a second, sealant layer the composition of which comprises a blend of a propyl ne polymer and a styrene ethylene butylene styrene copolymer; and

(c) a third adhesive layer adhering the first and second layers together with good adhesion, the third layer being positioned between, and adhered, in face-to-face contact,to the first and second layers.

2. A film according to claim 1, wherein the third adhesive layer is a styrene ethylene butylene styrene copolymer or a carboxy modified polypropylene.

3. A film according to claim 1 or claim 2, wherein the first layer is a polyester or copolyester polymer.

4. A film according to claim 1 or claim 2, wherein the first layer is a polyether block amide copolymer.

5. A film according to claim 1 or claim 2, wherein said first layer is a glycol modified cyclohexanedimethanolcyclohexanedicarboxylate.

6. A film according to any of claims 1 to 5, wherein the composition of the second, sealant layer comprises a blend of about 40% by weight to about 90% by weight of the said polypropylene and about 60% by weight to about 10% by weight of the said styrene ethylene butylene styrene copolymer.

7. A package made from a multiple layer film according to any of claims 1 to 6.

8. A package according to claim 7, which has been subjected to processing conditions involving a temperature of about 250°F (121°C) for a period of at least about 10 minutes.

9. A package made from a film according to any of claims 1 to 6, or a package according to claim 7 or claim 8, wherein said package is filled with and contains medical products including liquids and powders.

FIG.1

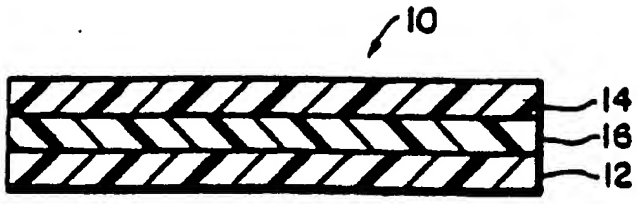


FIG.2

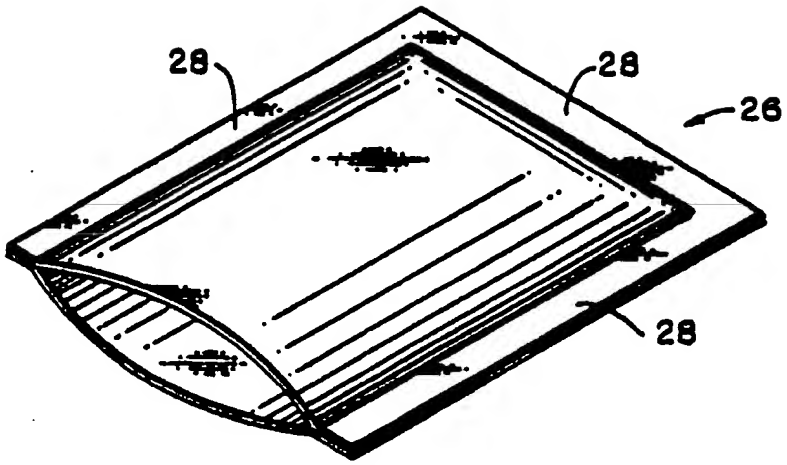
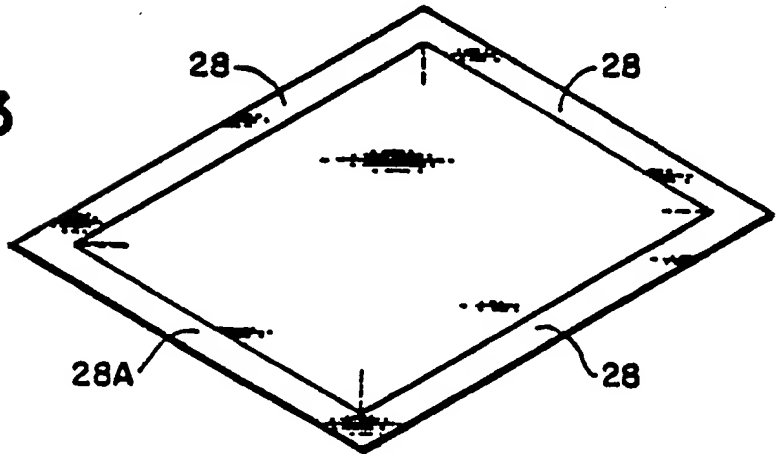


FIG.3



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EUROPEAN SEARCH REPORT

Application number

EP 86 30 9315

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
A	DE-A-1 629 791 (ZELLSTOFFFABRIK WALDHOF) * Claims 3,6 * -----	1,3,7	B 32 B 27/32 B 32 B 27/36 C 08 L 23/10

TECHNICAL FIELDS SEARCHED (Int. Cl.4)

B 32 B
C 08 L

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	13-04-1987	VAN THIELEN J.B.

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